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SHORT REPORTS

STRUCTURE OF NEW AMIDE FROM *PIPER OFFICINARUM*

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Key Word Index—*Piper officinarum*; Piperaceae; *N*-isobutyl-trideca 13-(3,4, methylenedioxyphenyl)-2,4,12-trienamide.

We have reported the presence of methyl piperate in the fruits of *Piper officinarum* [1] and now wish to report the structure of a new amide from the same source. The petrol extract of the fruits, on repeated column chromatography over neutral alumina, gave crystalline needles mp 112–113. The compound analysed for $C_{24}H_{33}NO_3$ (found C, 75·20; H, 8·75; N, 3·79; calc. for $C_{24}H_{33}NO_3$: C, 75·19; H, 8·62 and N, 3·66%). UV(MeOH) λ_{max} 259 nm, indicating the probable presence of a conjugated system related to sorbamide [2,3]. IR (KBr) showed characteristic bands for –NH, (3290, 3060 cm^{-1}), –C=O (1625 cm^{-1}), –C=C– (1660, 1620 cm^{-1}), –[CH=CH]$_2$–, (997 cm^{-1}) and no peak in the region 960–965 cm^{-1}; indicating the presence of *trans* 2-*trans*-4 dienamide system [2,3]. The NMR ($CDCl_3$) spectrum showed a large doublet 0·9 δ (6H, –C(CH_3)$_2$, *J*, 6H_z), a broad singlet at 1·37 (8H, [CH_2]$_4$), a multiplet between 1·9–2·4 (4H, allylic methylenes), a triplet at 3·19 (2H, N–CH_2–C–) typical for isobutyl amides; a singlet at 5·9 (2H, O–H_2C–O), multiplets between 5·7 to 6·2 (5H, olefinic protons, conjugated), doublet at 6·8 (3H, aromatic protons) and between δ 7–7·4 (IH, olefinic proton).

MS of the compound with fragments at 383, (M^+), *m/e* 161, 152, 73 and 148 supported its structure as the isobutylamide of 13-(3,4-methylenedioxy-phenyl)-tridec-2,4,12-enoic acid. On hydrogenation (Pd/c) the compound quickly absorbed 3 moles of H_2 to give the hexahydro derivative, mp 84–85° which on hydrolysis with HCl in alcohol in a sealed tube, gave isobutylamine hydrochloride mp 172°. The compound is therefore identified as *N*-isobutyl-trideca 13-(3,4, methylenedioxyphenyl): 2,4,12-trienamide.

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SESQUITERPENE ALCOHOLS IN CAMPHOR OIL

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Key Word Index—*Cinnamomum camphora*; Lauraceae; cadinenol; epicubenol; sesquiterpene alcohols.

Previous work. Non-volatile sesquiterpenoids in the leaves of the Camphor Tree [1].

Present work. Sesquiterpene alcohols have been investigated in camphor oil by many previous workers; the following were isolated from "blue oil" [2] which was prepared by the distillation of camphor oil at high temperature: α-cadinol, elemol, guaiol, β-eudesmol, juniper camphor, kusunol, campherenol and campherenone (ketone) [3–5]. Such conditions, however, may bring about thermal isomerization, dehydration, dehydrogenation, etc. to thermolabile components, so we have reinvestigated camphor oil which was isolated under less drastic conditions.

Monoterpenes, camphor and safrole were removed from the oil by distillation under reduced pressure (below 100°) and the residue was fractionated by chromatography on Si gel with *n*-hexane containing 0 ~ 50% EtOAc, preparative GLC, and TLC on Si gel; it was

confirmed that the compounds isolated by preparative GLC were not thermally altered during the separation, by means of TLC and/or IR.

α-[6] and β-Bisabolol [7], *t*-cadinol [8], cubenol [9], *t*-muurolol [8], (–)junenol [10], nerolidol, (+) cadinenol (**1**) [11], and epicubenol (**2**) [9] were isolated and identified by means of spectral data, GLC (R*t*) and other physico-chemical properties, along with the above mentioned components.

Among them, (**1**) (mp at 75°C, $[\alpha]_D$ = + 5·9) and (**2**) (liquid, $[\alpha]_D$ = −89·6) had almost identical IR-, NMR- and MS, but the ^{13}C-NMR-spectrum of (**1**) differs from that of (**2**); the main difference being a signal at 29·7 ppm in the ^{13}C-NMR-spectrum of (**1**) which is not found in that of (**2**).

Cadinenol has been isolated by several researchers [10,12–14], but there are slight differences in $[\alpha]_D$ among these isolates. Tomita and Hirose obtained a crystalline sesquiterpene alcohol from *Juniperus rigida* (mp 75°, $[\alpha]_D \pm 0$), the IR- and NMR-spectra of which were identical with those of epicubenol and cadinenol, and they identified it as (±) epicubenol [15]; in that report, they also said that it was identical with cadinenol.

From our experiments, however, we conclude that cadinenol is not identical with (±) epicubenol by reason of separation of (**1**) and (**2**) from each other chromatographically and by their having different ^{13}C-NMR-spectra.

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ASATONE IN PLANTS OF THE ARISTOLOCHIACEAE

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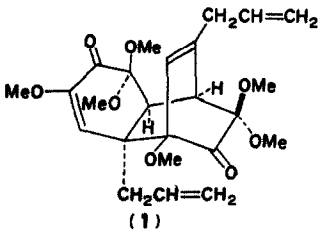
Key Word Index—*Asarum*, *Asiasarum* and *Heterotropa* spp; Aristolochiaceae; asatone.

Chemotaxonomic studies on species of *Asarum*, *Asiasarum* and *Heterotropa* have been extensively carried out particularly by Saiki and his co-workers [1]. In most cases, however, chemical constituents have been examined in steam-distillates of the fresh or air-dried leaves of the plant. Recently, we examined the chemical components in *n*-hexane extracts of *Asarum taitonense* Hayata (Taiton Kanaoi in Japanese) growing in Taiwan, and isolated two novel compounds, asatone (**1**) [2] and isoasatone [3], in *ca* 0·2 and 0·001% yields, respectively.



(**1**)

From the chemotaxonomic view point, it seemed useful to examine other species of *Asarum*, *Asiasarum* and *Heterotropa*, to see if they also contain asatone (**1**). We examined eighteen species, and isolated asatone (**1**) from four, (Group A below), by the following general procedure. Fresh leaves of *Heterotropa takaoi* F. Maekawa (200 g) were disintegrated into *n*-hexane (500 ml × 2) and left at room temp. for 1 week, and the filtrate concentrated under reduced pressure to yield a yellow oil, which on treatment with small amounts of *n*-hexane afforded white crystals (105 mg) of asatone (mp, IR and MS). The mother liquor was concentrated and subjected to preparative TLC (Kieselgel 60 PF_{254}) using *n*-hexane–EtOAc (3:1) to give three main compounds, safrol (20 mg), elemicin (73 mg) and asatone (113 mg). The leaf residue was further extracted with MeOH (500 ml × 2) at room temp. for a week to give a greenish-brown oil (350 mg), which by preparative TLC gave further quantities of the three compounds. In total, safrol, elemicin and asatone (**1**) were obtained from the fresh plant in 0·018, 0·066 and 0·15% yields, respectively.

The 14 other plants in which no asatone could be detected are shown in Group B.

Group A: *Heterotropa nipponica var. brachypodion* F. Maekawa (0·18%)*§; *H. takaoi* F. Maekawa (0·15%)*‖;

* Fresh leaf material. The other air-dried materials were kindly supplied by Prof. Y. Saiki (Shizuoka College of Pharmacy), and their sources and chemical components of the steam-distillates are cited in reference [1]. § Collected in Gifu-ken in middle of September. ‖ Collected in Aichi-ken in middle of September. † Collected in Aichi-ken late in August.